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# Combined Atomistic and Semi-Continuum Modelling of Nanoionic Space Charge Regions

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## Context

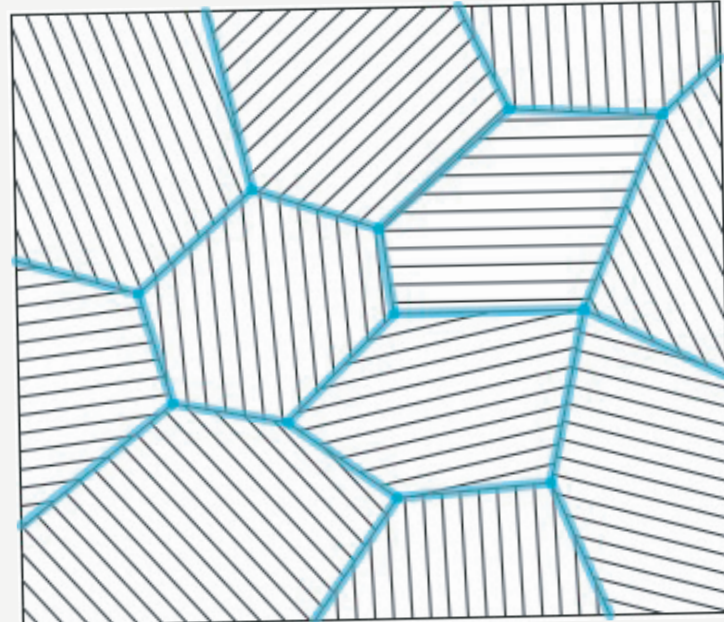
Solid electrolytes are interesting materials because they exhibit high ionic conductivities. Many solids exhibit electronic conductivities, but negligible ionic conductivities. This enhanced ionic conductivity makes solid electrolytes desirable for many different applications, such as solid oxide fuel cells.

Solid electrolytes are typically polycrystalline, with grain boundaries separating the different crystal regions. The structural distortion and change in Madelung potentials at these grain boundaries alters the defect segregation energies, leading to the formation of space charge regions. In space charge regions, defects are depleted or accumulated, which impacts the ionic conductivity. The overall ionic conductivity of a solid electrolyte therefore depends on both the bulk and grain boundary properties.

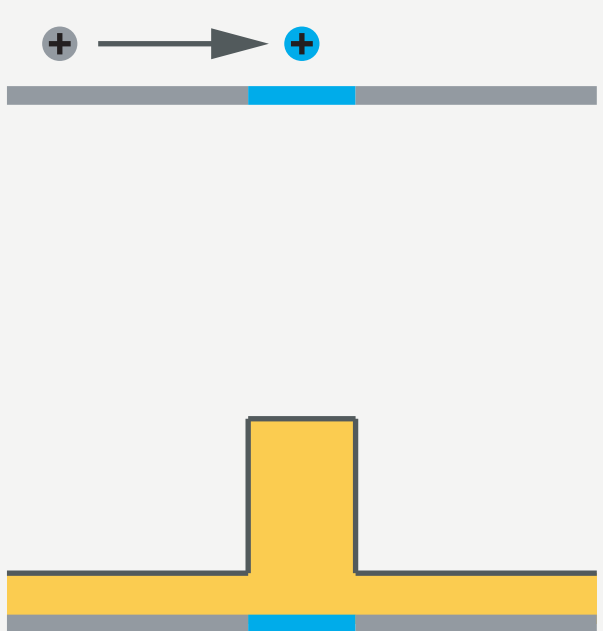
In materials with interfacial separations of the order of nanometers, space charge regions are expected to overlap producing 'nano-ionic' effects. These nano-ionic effects cause defect concentrations to locally deviate from bulk values. In certain cases, this is predicted to have a large effect on the ionic conductivity. The direct effect of space charge overlap on ionic conductivities is, however, difficult to quantify.

## Grain boundaries and space charge formation

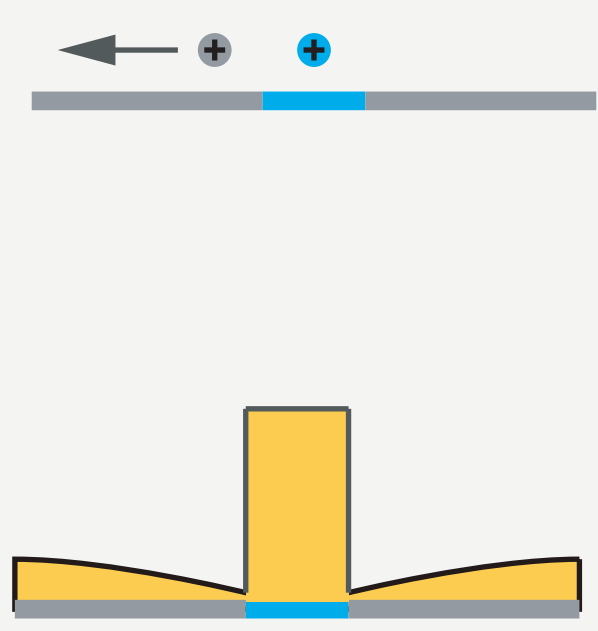
The structural distortion at grain boundaries affects defect concentrations and mobilities causing macroscopic ionic conductivities to differ from single-crystal values.



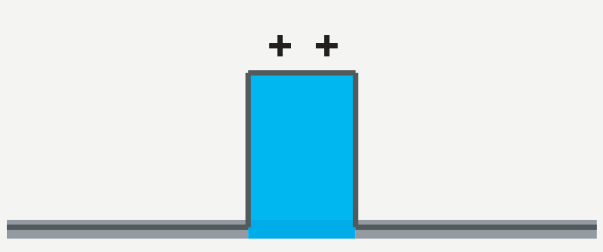
$$\sigma = nq\mu$$



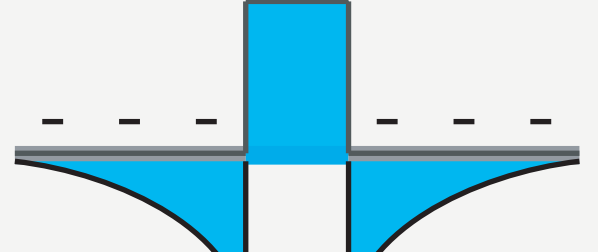
Distribution of non-interacting independent defects depends on segregation energies.



Distribution of interacting independent defects depends on electrostatic energies.



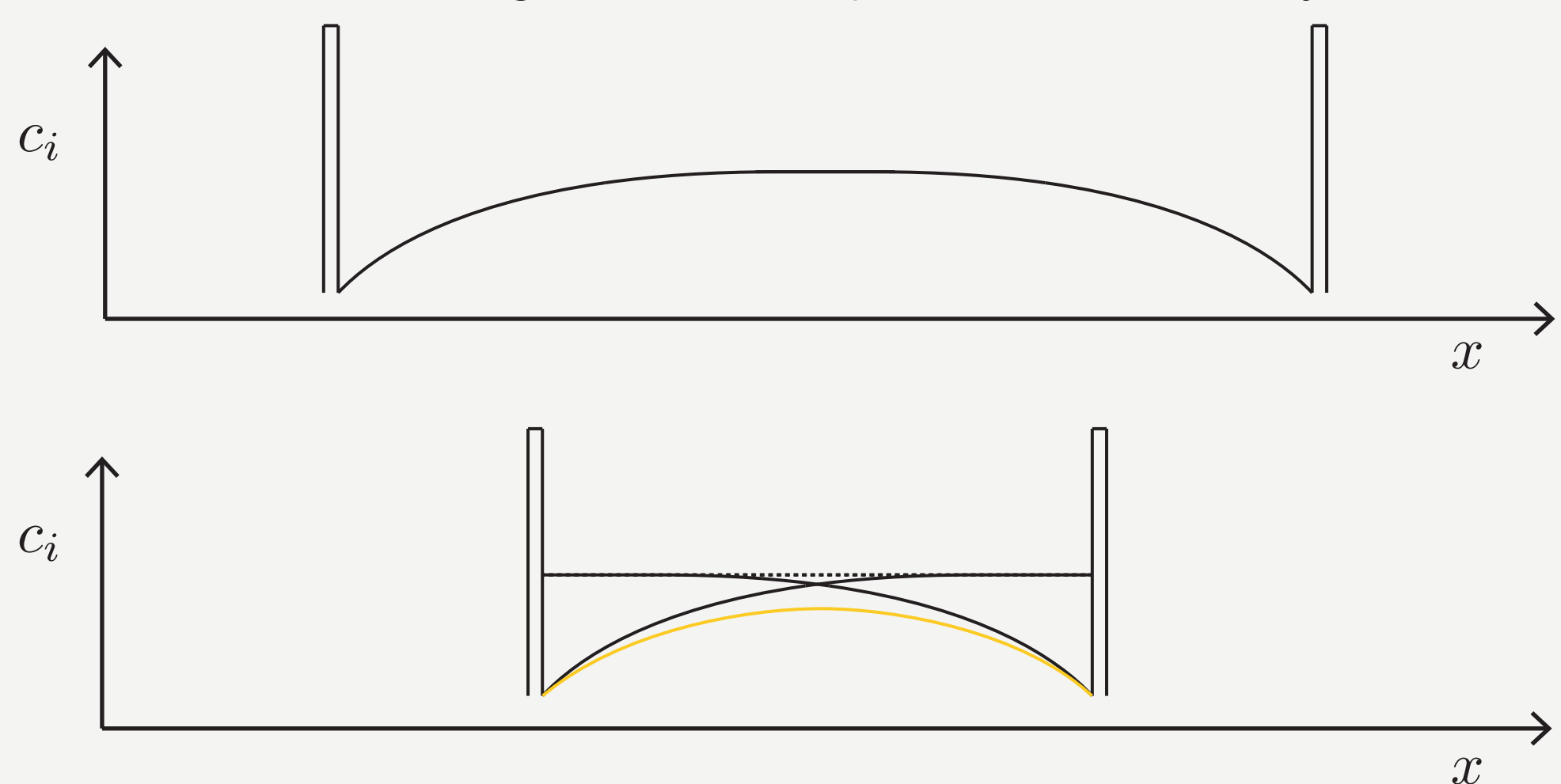
Grain boundary core carries a net charge.



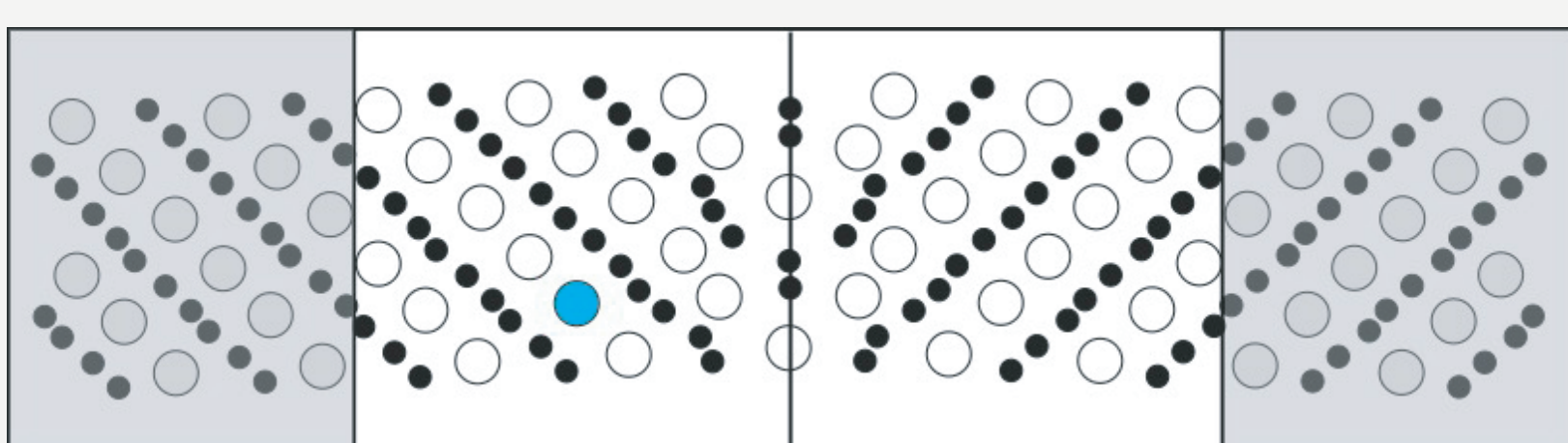
Regions adjacent to grain boundaries carry charge. (Space charge regions)

## Nano-ionic effects predicted at small grain boundary separations

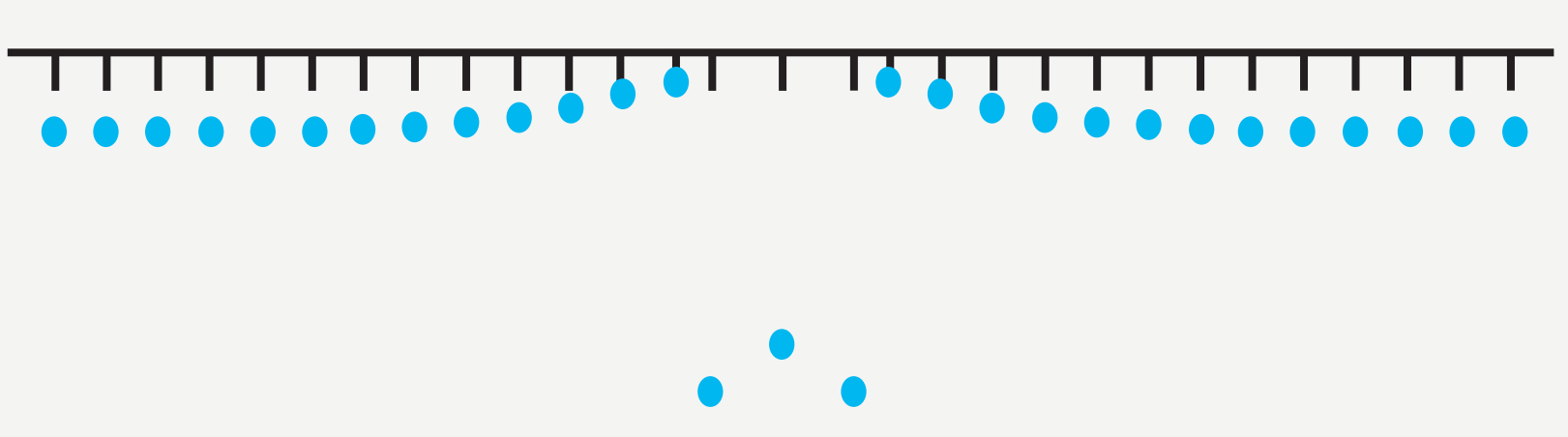
Where grain boundaries are sufficiently separated and the charge decays into the bulk between the grain boundaries, they are expected to behave as single grain boundaries. However when grain boundaries come into such proximity that the space charges overlap it is expected that the depletion effect will be enhanced. While this concept has been discussed, the effect of grain boundary separations in the nano-regime on the depletion and resistivity has not been quantified.



## Atomistic and semi continuum modelling of space charge



Atomistic calculations were performed using METADISE and CHAOS to calculate the explicit defect positions and segregation energies.



Defect segregation energies are mapped onto a 1D grid using atomistic positions.

Calculate defect concentrations. (Boltzmann equation)  
↓  
Calculate charge densities.  
↓  
Calculate electrostatic potential. (Poisson's equation)

$$c_i = c_{\infty} \exp\left(\frac{\Delta E_i + q\Phi_i}{kT}\right)$$

$$\rho_i = \sum_j q_j c_{j,i}$$

$$\nabla^2 \Phi = -\frac{\rho}{\epsilon}$$

The 1D Poisson-Boltzmann equation is then solved self-consistently using a finite difference approximation until a convergence limit is met.

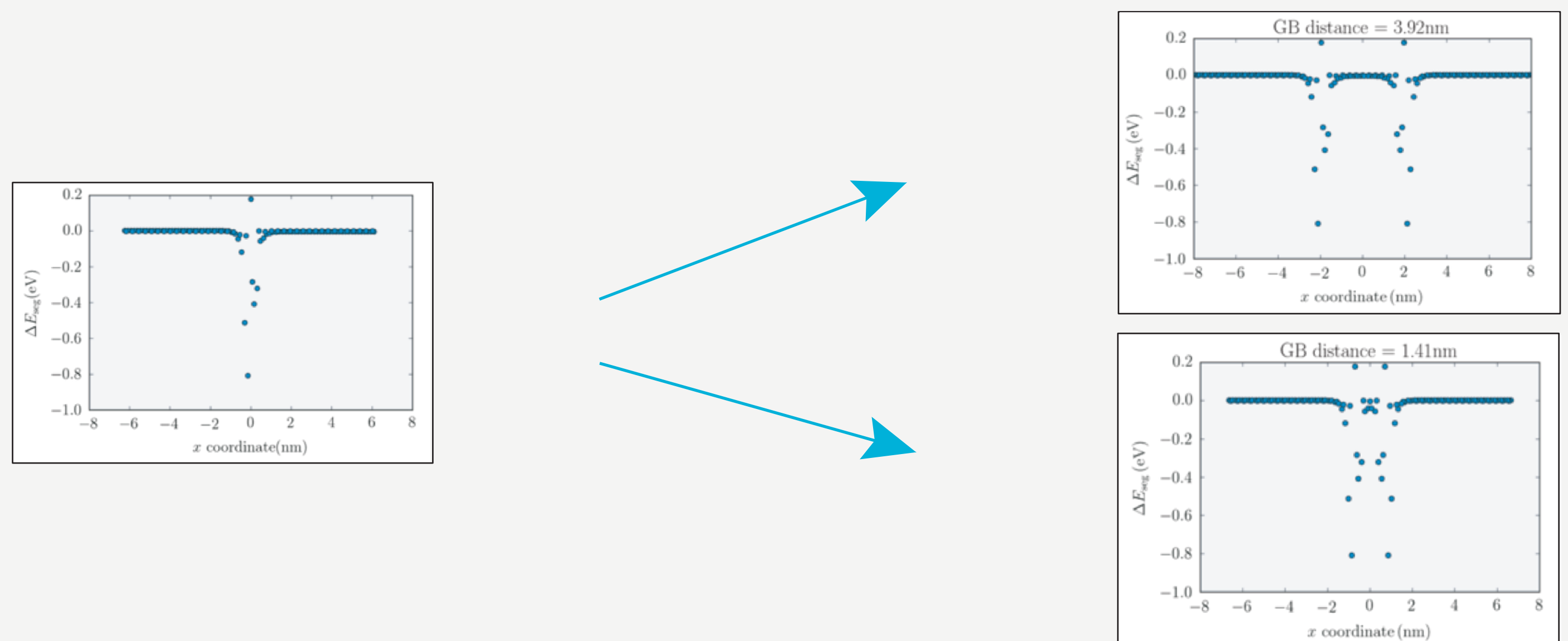
## Abstract

To quantify the effect of interfacial separation on space charge behaviour and ionic conductivities, we have performed numerical simulations of the defect distribution at the (111) grain boundary in Gd-doped CeO<sub>2</sub>. These grain boundaries were first modelled using classical interatomic potentials, to calculate atomically resolved defect positions and defect segregation energies. These coordinates and segregation energies were used as the input for a 1D-Poisson-Boltzmann solver used to calculate the space charge potential and self-consistent defect profile.

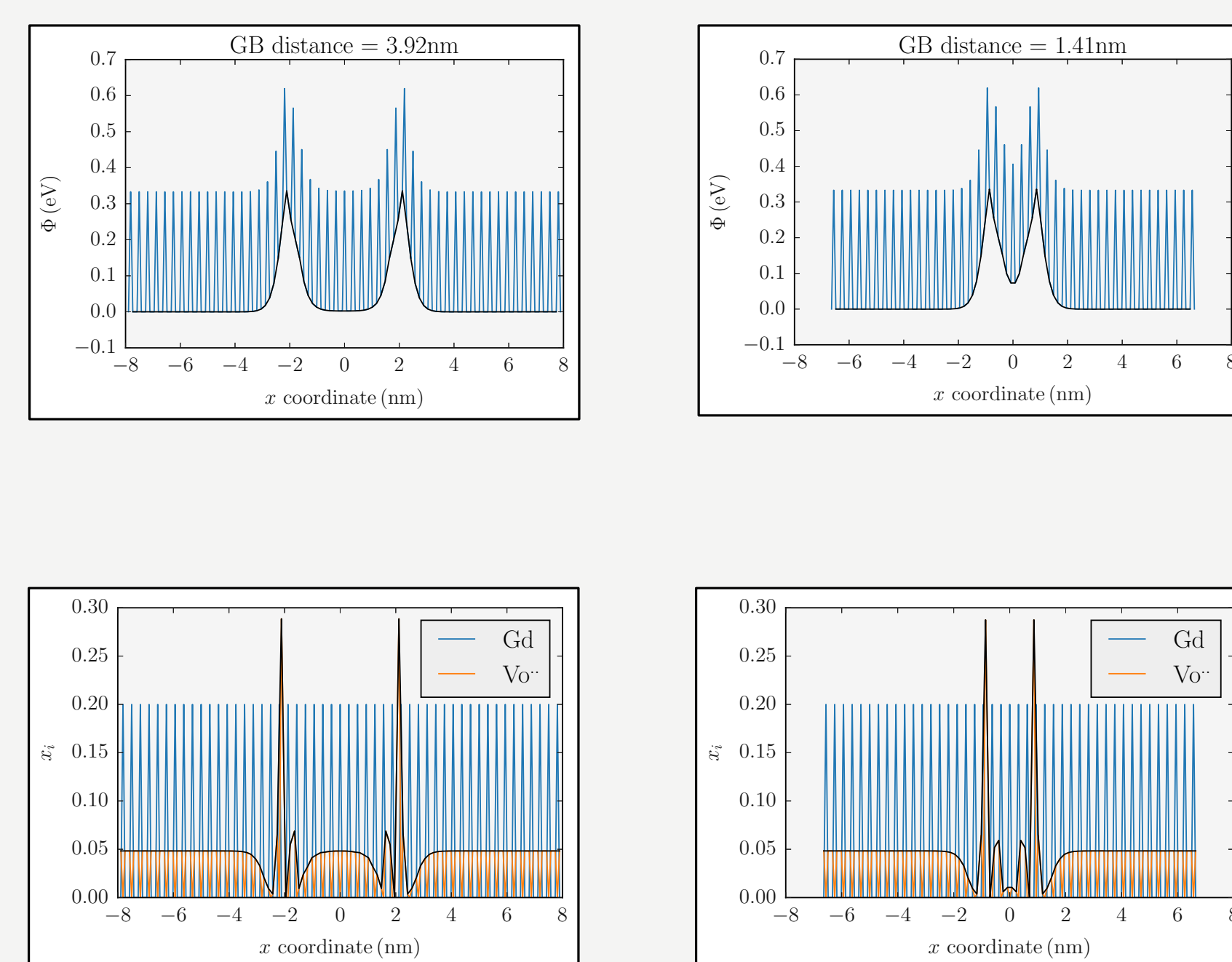
We find that as the interfacial separation is reduced, the depletion of oxygen vacancies is increased in the region between the grain boundaries. This enhanced depletion causes a decrease in the ionic conductivity over the system.

## Modelling space charge overlap in Gd-doped CeO<sub>2</sub> for the (111) grain boundary

The segregation energies generated from atomistic calculations are mirrored to create segregation energy profiles for dual grain boundary systems. Different grain boundary separations are generated by selecting sites with differing x coordinates as the midpoint of the mirrored system,



The segregation energies and atomic positions for the dual grain boundary system are used as the input for the Poisson-Boltzmann solver. We assume Mott-Schottky conditions by fixing the Gd concentration across the system and run the solver to generate the potential and defect distribution profiles.

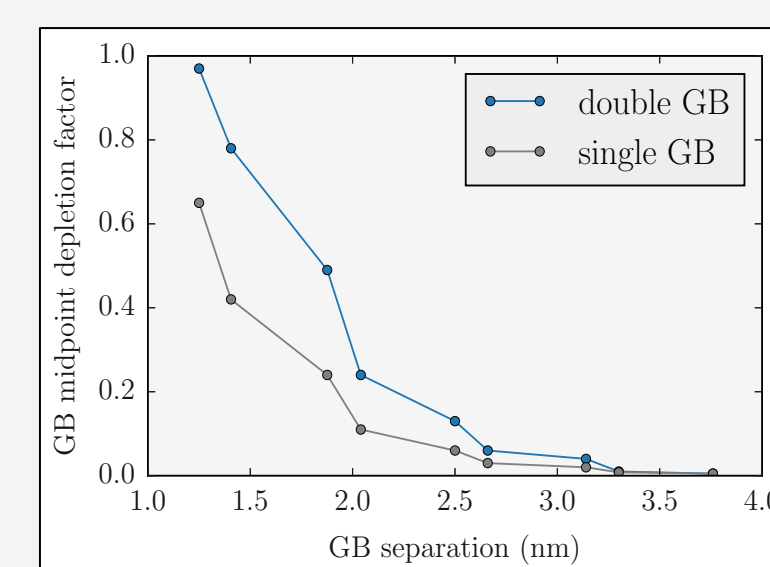


Comparing two dual grain boundary systems, a well separated system with a grain boundary separation of 3.92 nm and an overlapping system with a grain boundary separation of 1.41 nm the effect on the space charge overlap on the potential and defect mole fractions can be observed.

The region between the grain boundaries maintains a positive potential when the space charge regions overlap resulting in an enhanced depletion of the oxygen vacancies.

## Calculating the grain boundary resistivity and depletion factor

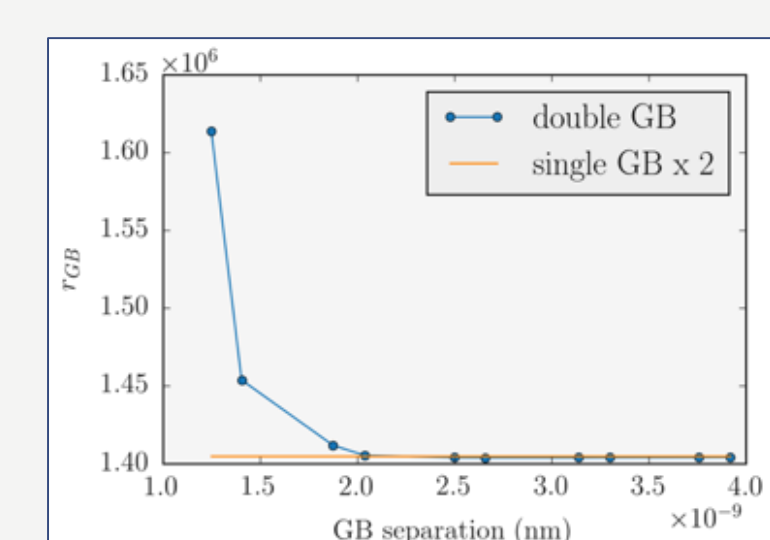
We define a 'depletion factor' to quantify the strength of the nano-ionic effect for a series of grain boundary separations and compare this to the equivalent point in the system with a single grain boundary.



$$D_i^s = 1 - \left(\frac{c_i}{c_{\infty}}\right)$$

As the grain boundary separation is decreased the region between the two grain boundaries becomes significantly more depleted.

The nano-ionic effect can also be quantified by calculating the grain boundary resistivity by taking each site as a resistor in series.



$$\rho_{\text{total}} = \frac{1}{\sigma_{\text{total}}} = \frac{1}{\sum \sigma_i}$$

$$\rho_{\text{total}} = \rho_1 + \rho_2 + \rho_3 + \rho_4$$

$$r_{GB} = \sum \rho_i = \sum \frac{\Delta x_i}{c_i}$$

As the grain boundary separation is decreased the grain boundary resistivity is increased significantly over a single grain boundary system.

## Conclusion

A combined atomistic and semi-continuum model was employed to quantify the nano-ionic effect in Gd-doped CeO<sub>2</sub>. It was found that as the grain boundary separation is decreased, the oxygen vacancy depletion is increased between the grain boundaries, resulting in an increased resistivity over the system.

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